

The corrosion and bioactivity behavior of SiC doped hydroxyapatite for dental applications

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Received 16 June 2014; received in revised form 21 July 2014; accepted 22 July 2014

Available online 31 July 2014

Abstract

Hydroxyapatite (HAP) coatings are commonly used to improve the bioactivity of Ti alloy used for orthopedic or dental implants. Recently, in order to decrease the dissolution rate and to improve the mechanical and anticorrosive properties, as well as the osseointegration of the HAP coated titanium alloy, the addition of different elements (Si or Ti) into HAP films was proposed.

The goal of this work was to enhance the bioactivity and corrosion resistance of HAP films by SiC addition. The coatings were deposited on Ti₆Al₄V alloy substrates by co-sputtering of HAP and SiC targets in a magnetron sputtering system. The films were characterized in terms of elemental composition, morphology and corrosion resistance in artificial saliva by EDS, SEM, and electrochemical techniques, respectively. The coatings were proposed to be used in dental applications. For this reason, in vitro bioactivity was investigated after 24 h immersion in artificial saliva. The improvement of the bioactivity and corrosion behavior was demonstrated for HAP coatings enriched with SiC.

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Keywords: B. Porosity; C. Corrosion; D. Apatite; E. Biomedical applications

1. Introduction

The degenerative diseases, osteoporosis (weakening of the bones), osteoarthritis (inflammation in the bone joints) and trauma lead to degradation of the mechanical properties of the bones due to excessive loading or absence of normal biological self-healing process [1–3]. Artificial biomaterials are the solutions for these problems, as surgical implantation of these artificial biomaterials of appropriate shapes help in restoring the function of the otherwise functionally compromised structures. Metallic materials continue to play an essential role as biomaterials to assist in the repair or replacement of bone tissue that has become diseased or damaged [4]. Presently, the materials used for these applications are 316 L stainless steel and titanium-based alloys [5]. Unfortunately, these materials have exhibited tendencies to fail after long-term use due to

various reasons such as high modulus compared to that of bone, low corrosion resistance and lack of bioactivity [5]. Thus, the actual challenge in the dental and orthopedic surgery is to obtain devices with both structural and surface compatibility with the bone, along with good mechanical and physicochemical properties. But the difficulties are impressive, as the surface of such implants presents deterioration in time and lower bioactivity. In general, it is difficult for a single material to possess all the required properties for the biomedical applications.

Recently, to promote the surface compatibility of dental or orthopedic implants and to generate osteoinductive character (which stimulates the formation of new bone cells), the implant surfaces were modified by (a) addition of materials of desired functions to the surface, e.g. bioactive ceramic coatings [6–8]; (b) conversion of the existing surface into more desirable chemistries and/or topographies [9–10]; and (c) removal of material from the existing surface to create new relevant topographies [11,12]. To improve the osseointegration of the

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metallic implants used in the clinical practice, the bioactive ceramic coatings based calcium phosphate were deposited on implant surfaces by using high-temperature plasma-spraying, sol–gel, electrophoretic deposition, pulsed laser deposition, ion-beam deposition and micro-arc techniques [11–21]. Until now, certain hydroxyapatite (HAP) coatings on metallic biomaterial surfaces have been shown to improve the corrosion resistance and the bioactivity of the metallic surface [13], being prepared by different techniques [14–16]. These methods include plasma spraying [17,18], co-precipitation [19], sol–gel [20], magnetron sputtering [21], and alkali treatment of titanium surfaces to induce mineralization or direct precipitation of apatite in simulated body fluid [22]. Despite of this interest to obtain the hydroxyapatite coatings, there are some drawbacks that restrict the use of HAP in biomedical applications, such as low corrosion resistance, high dissolution rate and low mechanical properties between the HAP coating and metallic substrate [23,24].

The aim of the paper is to enhance the corrosion resistance and the bioactivity of the hydroxyapatite coatings by adding the SiC into the HAP structure. The SiC compound was selected due to its good resistance to harsh mechanical and chemical environments, low dissolution rate and high mechanical properties [25–27]. Moreover, SiC is chemically inert and is expected to possess good biocompatibility. In scientific literature has been reported that SiC coatings prepared by magnetron sputtering improved the corrosion resistance and the tribological performance of various steels [25,28,29].

The coatings were prepared by RF magnetron sputtering in an Ar atmosphere. The coatings are intended to be tested for dental implants usage. Therefore, the corrosion and bioactivity properties were investigated in artificial saliva.

2. Experimental details

The substrate used in this paper was Ti6Al4V alloy (10 mm diameter, Bibus Metals AG). The Ti alloy specimens were polished and ultrasonically cleaned in tetrachloroethylene and isopropyl alcohol then dried. Before deposition process, the Ti alloy and Si specimens were sputtered by using Ar⁺ bombardment (1 keV; 5 min).

The reactive magnetron sputtering technique was used to prepare the coatings, by using two cathodes made of HAP and SiC (99.9% purity, 1 in. diameter, Kurt J. Lesker Company). The deposition parameters were summarized in Table 1. The pure HAP coating was used as reference coating. The distance

between the cathodes and the substrate holder was approximately 12 mm.

The corrosion resistance was investigated by electrochemical tests in Fusayama artificial saliva solution (composition: NaCl 0.4 g/l; KCl 0.4 g/l; NaH₂PO₄ × H₂O 0.69 g/l; CaCl₂ × H₂O 0.79 g/l and urea 1.0 g/l, pH=7) at room temperature, using a VersaSTAT 3 Potentiostat/Galvanostat. In order to have an exposure area of 1 cm², the samples (working electrode) were put into a Teflon sample holder. The tests were conducted with a typical three-electrode cell, with a Pt and saturated calomel as counter and reference electrodes, respectively. All electrochemical measurements were carried out with a scanning rate of 0.1666 mV/s, according to the standard ASTM G 5–94 (reapproved 1999). The tests were repeated at least two times for each type of coating. The electrochemical tests involved the following measurement sequence:

- monitoring of the open-circuit potential (E_{OC}) for 2 h, immediately after immersion in the electrolyte;
- recording of the potentiodynamic polarization curves from -1 V to $+2$ V vs. SCE.

The corrosion resistance was evaluated by determining the corrosion potential ($E_{i=0}$) and the corrosion current density (i_{corr}). $E_{i=0}$ and i_{corr} were estimated by graphical extrapolation of the anodic and cathodic branches at overpotentials of about ± 50 mV. The polarization resistance (R_p) was determined from the potentiodynamic curves as the slope of the potential versus the current density plot at $i=0$.

In vitro bioactivity was estimated by monitoring the open circuit potential for 24 h in artificial saliva after the potentiodynamic tests. These experiments were done in order to find the time when the oxide layer is reformed after the corrosion attack. The elemental composition of these layers was carried out by using a scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (FEI InspectS). Surface morphologies before and after bioactivity tests were investigated by SEM microscopy.

3. Results and discussion

Corrosion resistance in artificial saliva.

The open circuit potential (E_{OCP}) is used to evaluated the nobility of the surfaces. The rise of E_{OCP} values towards the positive direction indicates that on the investigated surface is

Table 1
Deposition parameters of the coatings.

	Base pressure ($\times 10^{-4}$ Pa)	Ar pressure ($\times 10^{-1}$ Pa)	RF powers fed (W)		Substrate bias voltage (V)	Substrate temperature (°C)
			HAP cathode	SiC cathode		
HAP	1.3	6.6	50	–	–60	700
HAP+SiC-10			50	10		
HAP+SiC-15			50	15		
HAP+SiC-20			50	20		

formed a passive layer which indicates a better corrosion resistance [30,31]. The evolution of the open circuit potential during the first 2 h after immersion in the artificial saliva is presented in Fig. 1. First of all, one may observe that in the first hour of immersion, the coatings shows significant changes, demonstrating that their surfaces were affected by the electrolyte. Despite the E_{OCP} drops, after 1 h of immersion, the E_{OCP}

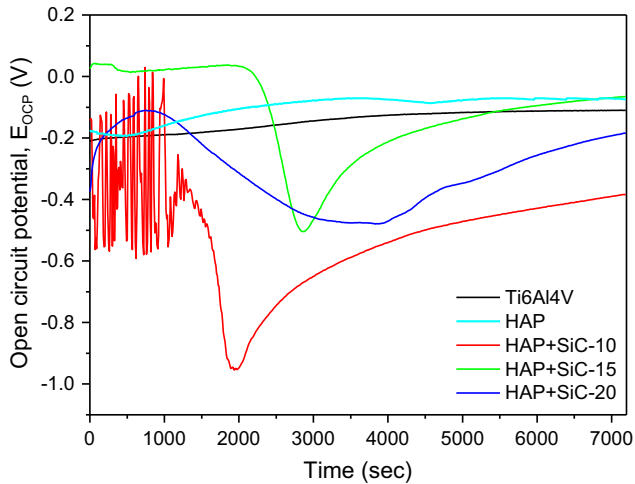


Fig. 1. Evolution of open circuit potential (E_{OCP}) vs. time during 2 h of immersion into artificial saliva solution with pH=7.

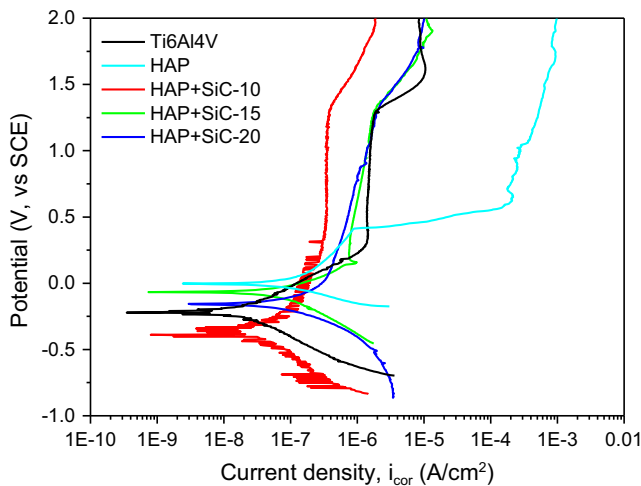


Fig. 2. Potentiodynamic polarization curves of the investigated samples into artificial saliva solution with pH=7, presented in logarithmic scale.

values increased, indicating formation of a passive layer on the surfaces. It can be seen that the HAP+SiC-15 coatings exhibited E_{OCP} values more electropositive compared to the uncoated substrate and the other coatings.

The potentiodynamic polarization curves of the uncoated and coated substrates are presented in Fig. 2. The electrochemical parameters, determined from the potentiodynamic curves, are presented in Table 2.

Various criteria have been proposed to evaluate the behavior of the materials at corrosive attack. First one is referred to the corrosion potential ($E_{i=0}$). A more positive value of $E_{i=0}$ indicates a better corrosion resistance [30,31]. The corrosion potentials ($E_{i=0}$) of the HAP+SiC-15 and HAP+SiC-20 coatings are higher than those of the uncoated titanium alloy, as a result of the beneficial barrier effect of these coatings. Between these two coatings, the HAP+SiC-15 exhibited more electropositive $E_{i=0}$, indicating that it is more resistant to saliva attack. The HAP+SiC-10 presented the most electronegative $E_{i=0}$ value, indicative of a poor corrosion resistance in saliva solution.

If we take into account the polarization resistance and corrosion current density parameters, the corrosion resistance of the materials is expected to be better if the R_p and the i_{cor} values are higher and lower, respectively [32].

For all samples, the R_p and i_{cor} values were higher and lower, respectively, in comparison with those of the uncoated substrate. From the point of view of this criterion, the

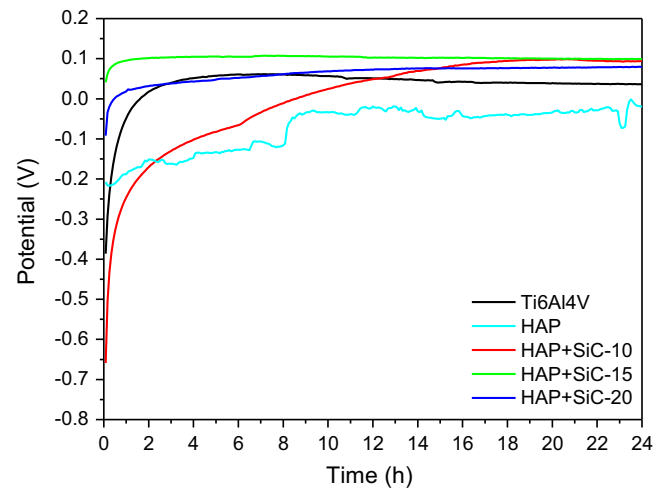


Fig. 3. Evolution of potential vs. time during 24 h of immersion in artificial saliva.

Table 2

Electrochemical parameters of the Ti₆Al₄V substrate and coatings: corrosion potential ($E_{i=0}$), corrosion current density (i_{cor}), polarization resistance (R_p), porosity (P) and protective efficiency (P_e).

Sample	$E_{i=0}$ (mV)	i_{cor} (nA/cm ²)	R_p (kΩ)	P	P_e (%)
Ti ₆ Al ₄ V	−215	287.8	5.06	–	–
HAP	−4	176.4	378.5	0.006	38.8
HAP+SiC-10	−368	281.7	19.31	0.157	2.1
HAP+SiC-15	−67	107.9	565.9	0.005	62.5
HAP+SiC-20	−157	133.2	490.9	0.009	53.7

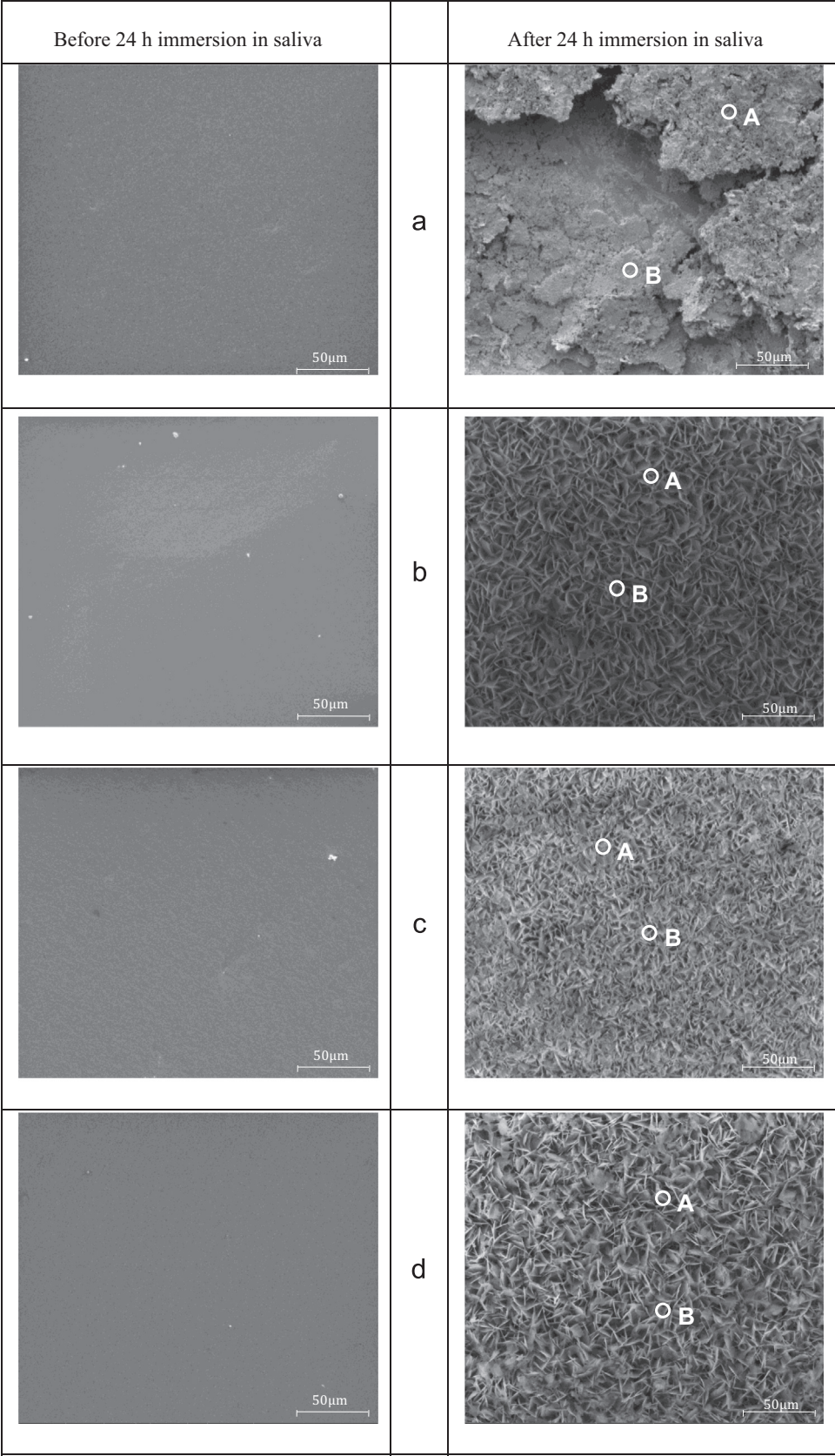


Fig. 4. SEM images of the coating surfaces before and after 24 h immersion in saliva: (a) HAP; (b) HAP+SiC-10; (c) HAP+SiC-15; and (d) HAP+SiC-20.

HAP+SiC-15 coatings show highest R_p and lowest i_{cor} values, demonstrating the best corrosion resistance.

Considering the criteria described above, it can be concluded that all of the coatings improved the corrosion resistance of the Ti₆Al₄V alloy. Comparing the electrochemical parameters, it appears that the HAP+SiC-15 coatings exhibited the most electropositive E_{corr} , the lowest i_{corr} and the highest R_p values, indicating superior corrosion resistance than the other coatings.

By using the electrochemical parameters calculated from potentiodynamic curves, the total porosity (P) of coating was estimated using Elsener's empirical equation [33]:

$$P = \left(\frac{R_{ps}}{R_p} \right) 10^{-\frac{|\Delta E_{i=0}|}{b_a}} \quad (1)$$

where R_{ps} and R_p are the polarization resistance of the substrate and of the coating, respectively, $\Delta E_{i=0}$ – the difference between the corrosion potentials of the coatings and of the substrates, and b_a is the anodic slope of the substrate.

As seen in Table 2, the HAP+SiC-15 and HAP+SiC-20 coatings exhibited lower porosity. The difference in porosity of these two coatings is no significant.

Also, the protective efficiency (P_e) was determined by using the following formula [34]:

$$P_e = \left(1 - \frac{i_{corr,coating}}{i_{corr,substrate}} \right) 100 \quad (2)$$

where $i_{corr, coatings}$ and $i_{corr, substrate}$ are the corrosion current densities of the coating and of the substrate, respectively.

Comparing the P_e values from Table 2, it should be observed that P_e increases with increasing RF power applied to SiC target from 10 W to 15 W, while a further power increase leads to a loss of the protective efficiency. Obtained results showed that the HAP+SiC-15 coating performed the best, the corresponding P_e value being of about 62.5%.

Bioactivity in artificial saliva.

After the potentiodynamic tests, the open circuit potential was monitored for all the samples in order to find out how long does it take to reform the oxide layer after the corrosion attack. The increase of the potential toward more positive values is often associated to the formation of a protective passive film at the

material surface [35,36]. In Fig. 3, the evolution in time of the passive layer is presented. One may observe that the time taken to reach the steady OCP is different and dependent on the type of the sample. In all cases, the potential is observed to change from more negative potentials to more positive potentials indicating the formation of the stable oxide layer. The coatings exhibited more electropositive E_{oc} values than the uncoated substrate. The potential of the HAP-SiC-15 sample reached constant values after 1 h, showing the formation of the more protective layers. One may observe that a stable oxide layer was formed on the coating surfaces in short time.

Morphology after bioactivity tests.

SEM micrographs of the coated samples before and after 24 h of immersion in artificial saliva are shown in Fig. 4. SEM micrographs showed a typical morphology for the calcium deficient HAP coating. All of the coatings were uniform formed on the substrate and exhibited crystalline leaflets that have nucleated and grown on the substrate surface. As can be seen, the morphologies of the HAP layers after 24 h of immersion in saliva are different to those of the as deposited coatings (Fig.4), where the presence of individual crystallites is not evident. Similar results were reported by other authors for the HAP coatings prepared by surface induced mineralization process [37,38].

Elemental composition after bioactivity tests.

The elemental compositions of the investigated coatings after 24 h of immersion are listed in Table 3. The data were obtained from two different locations on each surface as it was presented in Fig. 4. It is interesting to note that the coatings exhibited a Ca/P ratio close to 1.60, indicating the formation of the calcium deficient HAP film. Some authors suggested that the HAP with a Ca/P ratio of 1.60 is slightly more bioactive than stoichiometric HAP with a Ca/P ratio of 1.67 [39]. The as-deposited samples present a Ca/P ratio of about 1.67.

4. Conclusions

1. The HAP coatings with and without SiC addition were deposited on Ti₆Al₄V substrates by RF magnetron sputtering method in an Ar atmosphere at 700 °C substrate temperature.

Table 3

The EDS composition of the investigated coatings after 24 h immersion in saliva (pH=7).

Coating	Elemental composition (at%)			Ca/P
	O	Ca	P	
HAP				
Zone A	57.2	26.4	16.4	1.61
Zone B	59.5	24.9	15.6	1.60
HAP+SiC-10				
Zone A	61.6	23.6	14.8	1.59
Zone B	58.9	25.3	15.8	1.60
HAP+SiC-15				
Zone A	59.5	24.9	15.6	1.60
Zone B	61.9	23.5	14.6	1.61
HAP+SiC-20				
Zone A	59.1	25.2	15.7	1.61
Zone B	63.1	22.7	14.2	1.60

2. All the coatings exhibited good corrosion resistance in artificial saliva with pH=7: low corrosion current density (from 100 A/cm² to 281 A/cm²), high polarization resistance (from 19 kΩ to 566 kΩ), low porosity (from 0.005 to 0.157) and high protective efficiency (max. 62.5%).
3. The best corrosion resistance was obtained for the sample HAP+SiC-15 coatings: more electropositive corrosion potential (−67 mV), low corrosion current density (107.9 nA/cm²), high polarization resistance (565.9 kΩ), low porosity (0.005), and high protective efficiency (62.5%).
4. The bioactivity test indicates that after 24 h of immersion of the coatings in saliva, the calcium deficient HAP films with Ca/P ratio close to 1.60 were formed.
5. Research carried out showed that the corrosion behavior of Ti₆Al₄V alloy into artificial saliva solution with pH=7 was improved by HAP deposition. Moreover, by SiC addition to the pure HAP structure, their corrosion resistance was enhanced.

Acknowledgments

The present research was financial supported by a Grant number PN-II-RU-TE-2011-3-0284 of the Romanian National Authority for Scientific Research (CNCS-UEFISCDI) and a bilateral cooperation Turkey–Romania Project (RO599/2013 and TUBITAK 112R020).

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